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Development of adsorption air-conditioning technology using modified activated carbon – A review

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ABSTRACT

Adsorption air-conditioning technology has attracted much attention recently due to its environmental friendly property. Some successes have been reported in the literature on the adsorption technology for air-conditioning applications. This paper presents an overview of the researches which had been carried out on adsorption refrigeration system with the commonly used adsorbent and adsorbate working pairs, solar adsorption refrigeration and adsorption technologies in automobile. Activated carbon has been widely used as the adsorbent in adsorption refrigeration system. However, one of the bottlenecks which prevent the improvement of the adsorption refrigeration technology using activated carbon is the use of the readily available commercial activated carbon without prior treatment, which has resulted in relatively lower performance as compared to the conventional absorption and vapour compression technologies. Various modification methods on activated carbon are thus discussed in this paper for future development and improvement of adsorption air-conditioning system.

Contents

1. Introduction

Refrigeration applications have become an integral part of the present day living. With the changing lifestyle, the demand and supply of refrigerant systems have gradually increased [1]. The interest in adsorption systems first started to increase in the 1970s due to the oil crisis. In the 1990s, with the increase in ecological problems related to the use of chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) as refrigerants and the increase in energy consumption worldwide, it has become more urgent to find ways to use the energy resources as efficient as possible. These refrigerants deplete the ozone layer and contribute greenhouse effect when released into the atmosphere [2]. The use of these stratospheric ozone-depleting substances (ODS) had led to

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serious efforts not only by research scientists and engineers but also by national and international administrations and financial institutions in the development of ozone-safe technologies [3]. International agreements have been signed since the protocol of Montreal in 1987 to reduce the emissions of these refrigerants. On 1st October 2000, European Commission Regulations 2037/2000 was implemented. This regulation treated the whole spectrum of control and phase-out schedule for all ozone depleting substances, especially for CFCs and HCFCs. It was indicated that all HCFCs will be banned for servicing and the existing systems will be banned for maintaining till 2015 [4]. Effort has also been done to develop other types of refrigeration technologies which are more eco-friendly, cost effective, simple in design, convenient and reliable, e.g., adsorption refrigeration, magnetic refrigeration and thermo-electric refrigeration [1].

For the last few decades, there has not been any significant increase in the efficiency of the existing compressor-based refrigeration (i.e., mechanical refrigeration) systems which had reached the maximum level of innovation [1]. An attractive alternative for cooling or air-conditioning applications is the solid–gas sorption heat powered cycles. This is due to its environmental benign characteristic and it can be powered by waste heat and solar energy [5]. According to Leite and Daguenet [6], solid adsorption systems showed some advantages compared with other devices. First and foremost, the adsorbent did not submit to any change of volume during the sorption process. As compared with liquid adsorption, solid adsorption systems did not need a rectifying column. Furthermore, the techniques allowed the cycling of a large amount of refrigerant fluid [6].

The possibility of using waste heat and solar energy to power the adsorption system will produce the most environmental friendly cooling alternative for a few aspects including ozone depletion potential, global warming potential and primary energy consumption. Hence, adsorption system can be a good alternative to conventional vapour-compression machines. Solar adsorption refrigeration is a technical success. However, it is not commercially competitive with either the conventional vapour compression or PV refrigerator. Further development research is still required for improvement in the existing design to increase the overall performance of the system and reduce the system unit cost [7].

1.1. Prototype development

Prototype development is a key procedure for commercial application. Various adsorption refrigeration prototypes have been developed. For example, carbon–methanol solar-power ice maker [8], zeolite–water/carbon methanol cascading heat pump [9], carbon–ammonia convective thermal-wave air-conditioning system [10], multi-effect complex compound ammonia sorption machine [11], thermal-wave heat pump [12], three-stage silica gel–water chiller [13] etc. These prototypes can be powered by low grade thermal sources such as solar energy, natural gas and waste heat [14].

A laboratory prototype of adsorption cooling machine has been designed by Tamainot and Critoph [15] to demonstrate the effectiveness of the monolithic carbon–ammonia pair and the maximum specific cooling power over the whole cycle and the COP obtained were 60 W/kg and 0.12, respectively. The performance of activated carbon–methanol, zeolite–water and other working pairs were studied by Critoph and Vogel [16] and Meunier [17]. The results showed that the activated carbon–methanol pair was an ideal working pair for solar energy as it showed high COP and low generation temperature. Leite and Daguenet [6] also designed an adsorption system powered by solar energy which used activated carbon–methanol as the working pair, and it was found that the optimal COP of a transparent insulation material (TIM) cover system was 0.155.

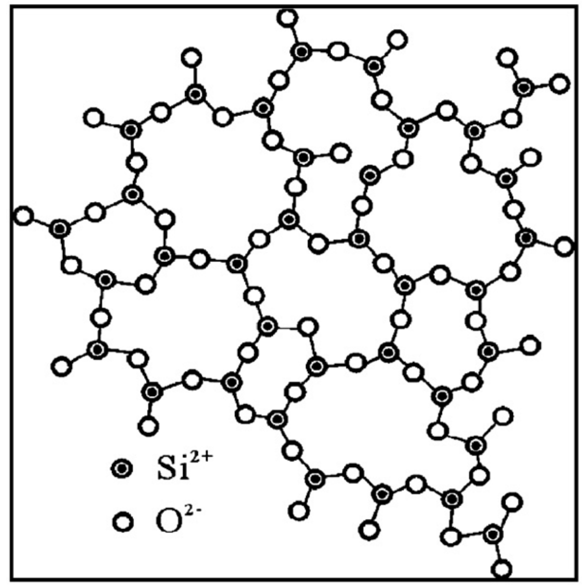

Fig. 1. Array of SiO_4 in silica gel [21].

According to Oertel and Fischer [18], agricultural production centres in India are usually situated in areas where electricity supply for running refrigeration plant is either not available or not reliable. Under these circumstances, one of the feasible options for agricultural cold storage in rural India is the non-electric decentralized cold storage. One of the promising solutions to the problem is the solar assisted refrigeration with low grade heat input. Thus, in their work they decided to use a solar-hybrid (solar and biomass dual fuel engine waste heat) system. This system required electricity for pumping and controls. Solar is a zero emission technology and acts as a buffer as far as carbon dioxide emissions potential is concerned. As predicted by Meunier [19], the waste heat adsorptive air conditioning system might be a possible breakthrough.

2. Selection of adsorbent/adsorbate pair

There are three types of working adsorbate and adsorbent respectively, which are favoured for pairing in solid adsorption refrigeration technology presently, namely the ammonia, methanol and water as adsorbate and activated carbon, silica–gel and zeolite for adsorbent. The selection of any pair of adsorbent/adsorbate depends on certain desirable characteristics ranging from their thermodynamic and chemical properties to their physical properties and even to their costs or availability and the affinity for each other [20].

2.1. Type of solid adsorbent

2.1.1. Silica gel

Silica gel is a type of amorphous synthetic silica. It is a rigid, continuous net of colloidal silica, connected to very small grains of hydrated SiO_4 as shown in Fig. 1. The adsorption centre of silica gel is the hydroxyl group in the structure due to its polarity and the ability to form hydrogen bonds with polar oxides, such as water and alcohol. The adsorption ability of silica gel is greatly influenced by the polarity where one hydroxyl can adsorb one molecule of water [21].

Silica gel retains chemically bonded traces of water (about 5%). Its adsorption capacity will decrease if it is overheated and lose the

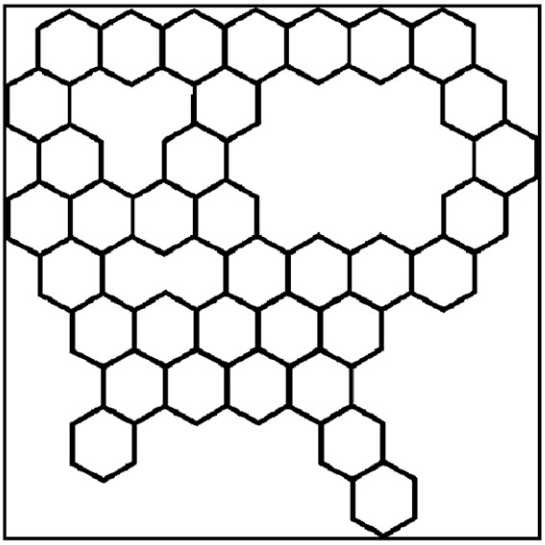

Fig. 2. Structure of activated carbon [21].

water. Consequently, silica gel is generally used in application with temperature below 200 °C. Silica gel is available in various pore size where the smaller the pore size, the greater the surface area per unit mass, which is typically 650 m^2/g. The pore diameter of common silica gel is 2, 3 nm (A type) and 0.7 nm (B type), and the specific surface area is about 100–1000 m^2/g. It is widely used for desiccation due to its large adsorption ability. The main difference between both types of silica gel is that type A silica gel can be used for all desiccation conditions but type B silica gel can only be used when the relative humidity is higher than 50% [3].

2.1.2. Activated carbon

Activated carbon can be made from materials such as wood, peat, coal, fossil oil, chark, bone, coconut shell and nut stone. The microcrystal for the activated carbon produced from bone is a six element carboatomic ring and the performance is influenced by the functional groups that are connected to the carboatomic ring [22]. The functional groups on the surface of activated carbon are different if the carbonaceous material and the activation method are different. Activated carbon is different from other types of adsorbent on the surface feature. The whole surface of activated carbon is covered by an oxide matrix and by some inorganic materials. Hence, it is non-polar or has a weak polarity. The heat of adsorption of activated carbon pair is lower than that of other types of physical adsorbent pairs [21]. The net structure of activated carbon has larger pore area at the surface of the grain and narrow pore area within the grain. The specific surface area of activated carbon is approximately 500–1500 m^2/g [23].

Activated carbon fibre is different as compared with granular activated carbon. It is generally used in the production of fabric such as cloth and tissue. Activated carbon fibre has better mass transfer performance as compared with the granular form of activated carbon. It has larger specific surface area and the pores are more uniform than the granular type. Besides that, activated carbon fibre has larger heat transfer performance. However, the anisotropic thermal conductivity and higher contact thermal resistance between the fibre and the adsorber wall result in the disadvantages of activated carbon fibre as compared with the granular activated carbon [24]. Fig. 2 shows the structure of activated carbon.

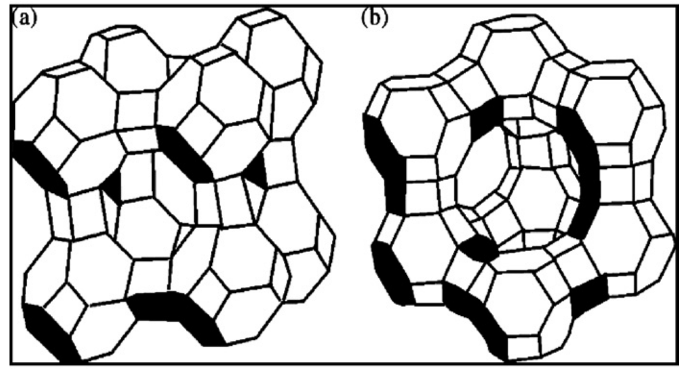

Fig. 3. Crystal cell unit of zeolite: (a) crystal cell unit of type A zeolite; (b) crystal cell unit of type X, Y zeolite or faujasite [23].

2.1.3. Zeolite

Zeolite is a type of aluminasilicate crystal composed of alkali or alkali soil [21]. It is natural mineral assemblies of SiO_4 and AlO_4 with precisely uniform crystal lattice. 30 kinds of zeolite crystals have been found in mines around the world. Many types of synthetic zeolites have been developed for special applications such as molecular sieves of types 4A, 5A, 10X and 13X, which have been developed by the Linde Co, USA [3]. The chemical formula of zeolite is:

$$M_{y/n}[(AlO_2)_y(SiO_2)_m]zH_2O \quad (1)$$

where y and m are integers and m/y is equal or larger than 1. n is the chemical valence of positive ion of M, z is the number of water molecule inside a crystal cell unit [21].

Fig. 3 shows the crystal cell unit of zeolite. The positive ion must have its electric charged balanced with the electric charged of aluminium atom. The net electric charge of each aluminium atom is −1. The aluminasilicate skeleton has a cage format, and it is usually connected by six casement section, which can adsorb a large amount of extra molecules [23].

The main types of natural zeolite for adsorption refrigeration are chabazite, sodium chabazite, cowlesite and faujasite. Zeolites can be artificially synthesized and they are named by one letter or a group of letters, such as type A, type X, type Y, and type ZSM [22]. Artificial zeolites have higher bulk specific weight and better heat transfer performance but they are more expensive than natural zeolites. The selectivity for different adsorbates are determined by the pore size of zeolites. The cage structure of the micropore makes the adsorption process to proceed in a small range, hence the zeolites are also named as zeolite molecular sieve. At temperature higher than 600 °C, most zeolite molecular sieves can be destructed [21].

2.2. Type of adsorbate

Presently, adsorption technology can be used not only for air-conditioning and refrigeration but also to upgrade heat with thermal transformer. The type of adsorbate selected should be according to the application. Ammonia, water and methanol are some common refrigerants for adsorption refrigeration system. Refrigerants can be divided into positive pressure refrigerants and vacuum refrigerants. Positive refrigerants are refrigerants with boiling point below 10 °C at 1 atm. One example of positive pressure refrigerant is ammonia. It can be used with chlorides, activated carbon and activated carbon fibre [25].

Methanol and ethanol have similar saturation pressure. Methanol is normally used in association with activated carbon or activated carbon fibre. Water can be considered as a perfect refrigerant except for its extremely low saturation pressure and

Table 1
Physical properties of common refrigerants for adsorption systems [21].

Refrigerants	Chemical formula	Normal boiling point (°C)	Molecular weight (g/mol)	Latent heat of vaporization, L (kJ/kg)	Density, r (kg/m^3)	$\rho \times L$ (MJ/m^3)
Ammonia	NH_3	34	17	1368	681	932
Water	H_2O	100	18	2258	958	2163
Methanol	CH_3OH	65	32	1102	791	872
Ethanol	C_2H_5OH	79	46	842	789	665

the impossibility to produce temperature below 0 °C. It is normally in pair with silica gel or zeolite. Some physical properties of refrigerants for adsorption systems are shown in Table 1 [21].

3. Adsorption

Adsorption is the general phenomenon based on a physical or chemical reaction process, resulting from the interaction between a solid (adsorbent) and a gas/liquid (refrigerant) [4]. Adsorption can be divided into physical adsorption, which is caused by the Van der Waals forces and chemical adsorption, in which a chemical reaction is involved. It is an exothermic process due to the gas–liquid phase change. The energy liberated depends on the nature of the adsorbent–adsorbate pair and is called the isosteric heat [6].

The atoms, molecules or ions in a liquid are diffused to the surface of a solid in a liquid phase adsorption. They are bonded with the solid surface or are held by weak intermolecular forces. In this case, the solid is defined as the adsorbent whereas the components being adsorbed are called solutes when they are in the liquid. The components form adsorbates upon adsorbed on the solid provided that the maximum adsorption capacity of the adsorbent is not exceeded [26].

Adsorbents like silica gel, zeolite and porous or active alumina have special affinity with polar substances like water. These adsorbents are termed hydrophilic. Non-polar adsorbents such as activated carbon, polymer adsorbent and silicate have more affinity for oil and gases than that for water and these substances are termed hydrophobic. Adsorption is the term for the enrichment of gaseous or dissolved substances (the adsorbate) on the boundary surface of a solid (the adsorbent). The active centres on their surface adsorbents are where the binding forces between the individual atoms of the solid structure are not completely saturated. At these centres, an adsorption of foreign molecules takes place. To understand the adsorptive solvent recovery, some fundamentals of adsorption and desorption must be considered, as shown in Fig. 4 [27].

3.1. Adsorption refrigeration

Cooling is the process of reducing the temperature of our surrounding or the temperature of a product for purposes of either comfort or preservation. Cooling can be obtained by different types of energy ranging from electrical to mechanical or even purely thermal energy such as fossil fuel derived, biomass derived or solar radiation [28]. There have been a lot of experiments carried out on refrigeration for the purpose of finding cheap methods to provide cold for preservation and storage of food. The use of vapour compression unit powered by electricity is the most common means of producing cold. However, this method is not applicable in rural areas because the non-availability of electricity has affected the standard of living at rural areas [29]. Originally, the adsorptive process is applied to chemical industrial processes such as gas separation and catalysis. Recently, heat pumps and refrigeration have been proposed as an alternative to vapour compression system. Adsorptive refrigeration systems have been proven to be well adapted to soft technology applications since it operates without moving parts and uses low grade thermal energy from residual heat and solar energy [6].

Refrigeration is of very great importance in our lives. It has numerous potential applications such as being the storage of food and preservation of vaccine [29]. The advantages of adsorption refrigeration systems are environmentally benign, zero ozone depletion potential (ODP) as well as zero global warming potential. These are due to the use of natural refrigerants such as ammonia, water, and methanol. The adsorption systems have less vibration, simple to be controlled, low initial investment and expenditure, and less noise as compared with the existing vapour compression and absorption systems. However, the most attractive part of this system is the efficient use of solar energy and low-grade waste heat [30].

3.2. History development of adsorption refrigeration

In 1848, Faraday was the first to discover vapour adsorption by using solid adsorbent. It was reported that the adsorption cycles for heat pumping or refrigeration was used in the early 1990s. The solid/vapour systems held great promise for overcoming the limitations of the engine-driven vapour compression and the liquid/vapour systems since they were commercialized in the 1920s. The solid or vapour adsorption cycle at that time was simple but inefficient [31]. Residential and commercial refrigeration systems were designed by Miller [32] using silica gel and sulfur dioxide. Until the mid-1970s, with the advent of the mechanical compressor and the application of CFCs which were more efficient, further investigation of the cycle was at a standstill.

In recent years, a lot of efforts have been done to develop energy efficient technologies to solve the global environmental problem. These ecological problems such as global warming and ozone depletion in the world have aroused scientists to develop energy utilization systems. Due to the relatively lower environmental impact and large energy saving potential, the adsorption heat pump/refrigeration systems have become very attractive as all these systems do not use either CFCs or HCFCs as working fluid. Additionally, fossil fuel or electricity is not used in these systems as driving heat source [33].

3.3. Solar adsorption refrigeration

Solar adsorption refrigeration devices are very important in remote areas for cooling requirements such as air-conditioning, ice-making and medical or food preservation. As a result of energy shortage, the use of solar energy for environmental control has been receiving much attention nowadays [34]. Various types of solar water heaters have been introduced such as the plate type, vacuum tube type, and heat pipe vacuum tube type. Besides, solar powered ice-makers using both absorption and adsorption systems have been demonstrated by some previous researchers [35].

According to Clausse et al. [36], one of the possible ways to reduce building fossil fuel consumption and greenhouse gas emission in low-energy building was the solar heating air-conditioning. The absorption, adsorption and dessicant cooling were three technologies that were currently available for solar heat-driven

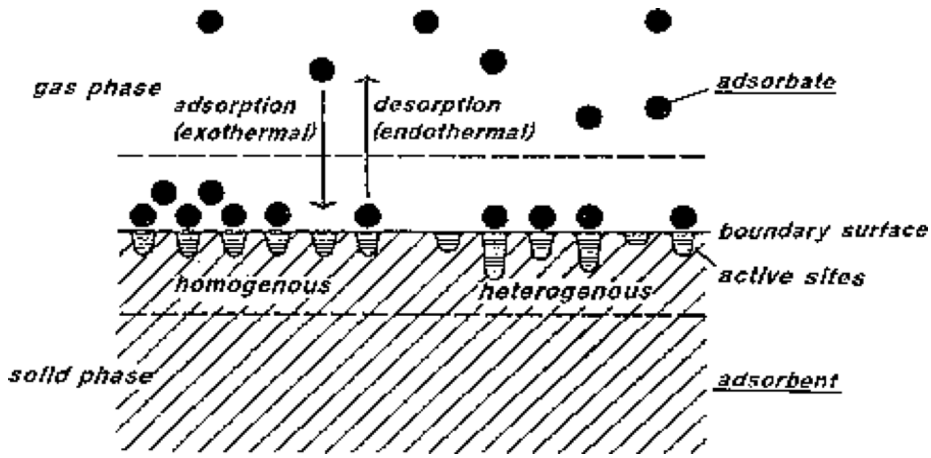

Fig. 4. Fundamentals of adsorption and desorption [27].

air-conditioning. Henning [37] made a comparison between the three different technologies and summarized that the absorption was the most widely used in Europe with 59% of the installed systems where adsorption and dessicant cooling was 11% and 23%, respectively. Clausse et al. [36] explored the possibility to perform heating and air-conditioning of state of the art building located near Paris in France by using solar adsorption air-conditioning during summer and direct heating during winter by means of an enhanced compound parabolic solar collector. They reported that the air-conditioning system showed promising results whereas the installation of the solar collector was able to heat the house most of the days. The installation of solar driven air-conditioning systems together with solar heating made the installation of solar collectors more attractive from a financial point of view [36].

Solar refrigeration is usually used for agricultural products storage, food and medicines in remote area. It has the potential to improve the quality of life of people who live in area with insufficient electricity. It is also noiseless, non-corrosive and environmentally friendly [34]. The applications of solar sorption systems can be broadly classified into three categories based on the cooling temperature demand: air-conditioning (8–15 °C) for spaces, refrigeration (0–8 °C) for food and vaccine storage, and freezing (<0 °C) for ice-making or congelation purposes [4]. One of the promising solar thermal refrigeration methods is the adsorption system. It is environmental friendly along with low cost and low maintenance needed. However, these systems are not yet ready to compete with the well-known vapour compression system due to the high capital costs [34].

When solar and conventional sources are compared to refrigeration or ice-production, there are two points of concern: First, the solar system has a very low COP, hence it is considered as bad thermal machine. Secondly, the solar system is more expensive than conventional system. Corbella and Garibotti [38] analysed the two statements and they concluded that their “second law COP” should be compared instead of the COP derived from the first law in order to make a comparison between a conventional and a solar powered system. Furthermore, they also concluded that the second statement was not true based on the inflation rate, future fuel prices and the distance from the fuel source to the system. They claimed that after considering the above factors, the solar system could be cheaper than the conventional system. Effort had been done to improve the system such as by reducing the collector area, improving the system performance and reducing the cost of solar components [34].

The current technology of adsorption solar-powered icemakers allows a daily ice production of between 4 and 7 kg/m^2 of solar collector, with a solar COP between 0.10 and 0.16 [39]. The cooling technologies available are continuous adsorption, intermittent adsorption, solid/gas adsorption, diffusion, absorption and desiccant systems [40]. According to Li et al. [41], due to the simple operation, the intermittent solid adsorption cycle provided a promising alternative for solar refrigeration. Two different working pairs were used in their work, the activated carbon–methanol pair and the activated carbon–ethanol pair. They concluded that the adsorbing and desorbing refrigerant amounts of the two working pairs gave different results in which the activated carbon–methanol pair was reported to be more superior in ice production.

In the work carried out by Anyanwu [7], there were three major components in solar-powered adsorption refrigeration, which were the container of adsorbents, condenser and evaporator. The adsorbent was packed in a black, sealed container for solar radiation absorption. During the day time, the container and the adsorbent were heated to the maximum cycle temperature by solar heat. The refrigerants started desorbing from the adsorbent at its condensing pressure corresponding to a particular temperature. Heat was dissipated to the surrounding as the refrigerant vapour was changed to liquid in the condenser. The condensate finally flowed into a liquid receiver or into the evaporator. During the night time, the pressure of the entire system reduced when the adsorbent was cooled to near ambient temperature. The refrigerant boiled in the evaporator when the adsorbent pressure equalled the saturated vapour pressure and caused the heat to be absorbed from the immediate environment. Cooling was produced when the refrigerant vapour was readsorbed into the adsorbent. Fig. 5 shows the intermittent adsorption solar refrigeration scheme.

A review made by Fan et al. [4] concluded that solar-powered sorption refrigeration technologies could be used for producing a wide range of temperature cold. It was not only used for refrigeration, air-conditioning applications and ice-making, but was also able to meet the demand for energy conservation and environment protection. They made comparison between absorption systems and adsorption systems. It was concluded that the absorption systems were more suitable for air-conditioning whereas adsorption systems were more employed for low temperature purpose.

Solar refrigeration is highly dependent upon environmental factors such as cooling water temperature, air temperature and solar radiation. The energetic conversion efficiency is low, and solar cooling and refrigeration are not yet competitive economically with the conventional systems. However, research activities in this sector are still increasing to solve the technical, economical and environmental problems [34].

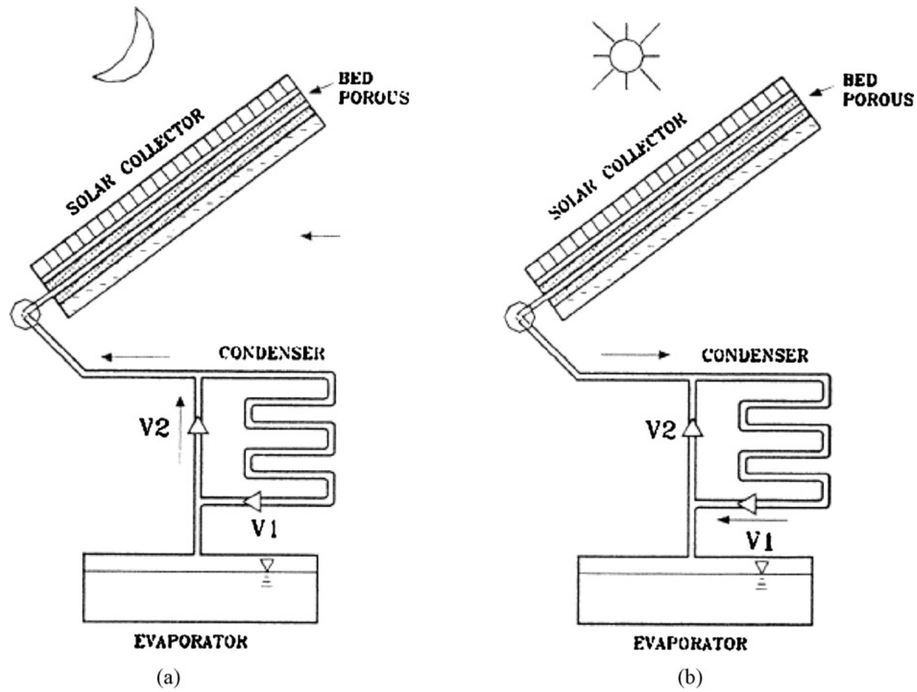

Fig. 5. Intermittent adsorption solar refrigerator scheme: (a) stage of cold production; (b) regeneration stage [6].

3.4. Adsorption cooling technologies in automobile

According to Zhang [42], the efficiency of diesel engine was about 35% whereas in the operation of water-cooled engine, about 35% and 30% of the input energy was wasted in the coolant and exhaust gases, respectively. The utilization of exhaust waste heat has turned out to be an attractive application since energy has become a major topic of discussion on natural resources preservation and cost reduction. It is vital to develop more efficient processes based on estimation of energy resources reduction at medium and long term. Substitution of the CFCs by alternative refrigerants is an important point according to the Montreal Protocol signed by 46 countries in 1987 which was after that being revised in 1990 to protect the ozone layer [43].

Generally, the conventional electrical-driven compression systems are widely used in almost all automobiles. The automobile air-conditioning systems were first designed to provide a comfortable driving condition throughout the journey [44]. As compared with mechanical vapour compression systems, the adsorption systems can save energy if powered by waste heat or solar energy. Besides, adsorption systems are simpler to control, has no vibration and lower operation costs. Additionally, the adsorption systems can be powered by a large range of heat source temperatures and it does not require a liquid pump or rectifier for the refrigerants as compared with the liquid absorption system. Other advantages of the adsorption systems are no corrosion problems and less sensitive to shocks and the installation position. This makes it suitable for application in locomotives, busses, boats and spacecrafts [2].

One of the potential energy sources for absorption refrigeration system is the internal combustion engine since one third of the energy available in the combustion process is wasted through the exhaust gas. The use of the exhaust gas in the absorption refrigeration system can increase the overall system efficiency [43]. Since the adsorptive systems usually have large volume and mass, vehicles that are more suitable for the adsorption refrigeration air-conditioning system are buses and locomotives [2].

Jiangzhou et al. [45] presented a novel adsorption air-conditioning system used in internal combustion engine locomotive driver cabin. Zeolite–water was used as working pair and it was driven by the waste heat from exhaust gas of internal combustion engine. The system consisted of an absorber and a cold storage evaporator. Space cooling could be obtained by continuously and steadily providing refrigeration capacity to the locomotive driver cabin. The experiment showed that the new type of system could meet the demand of air-conditioning for locomotive driver cabin and they believed that more refrigeration capacity might be output if adsorber cooling condition of prototype machine could be greatly improved. The schematic diagram of locomotive driver cabin air-conditioner is shown in Fig. 6. In desorption phase, the exhaust gas passed through the adsorber. The refrigerant vapour was produced and entered the air-cooled condenser. The refrigerant flowed into the evaporator. In adsorption phase, the exhaust gas passed through chimney and entered the atmosphere while the air flowed into the adsorber. The refrigerant vapour was adsorbed by adsorbent and the refrigeration capacity was produced in the evaporator. The condensing heat and adsorption heat was discharged into the

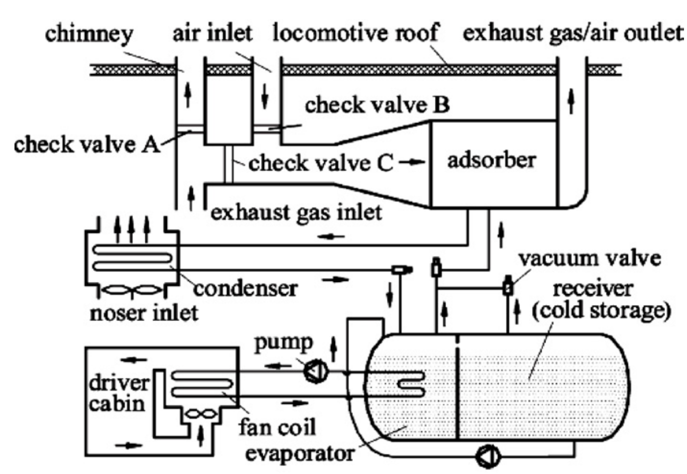

Fig. 6. Schematic diagram of locomotive driver cabin air-conditioner [45].

atmosphere. The refrigeration capacity was then sent to the fan-coil in the driver cabin by chilled water for space cooling [45].

Zhang [42] studied the adsorption air-conditioning system generated by the exhaust gases of a bus. There were two concentric pipes in the adsorber and the exhaust gases or the cooling air released or removed heat through the inner pipes. Zeolite was used as adsorbent and placed between the inner and the outer pipe. Water was used as refrigerant and fins were attached to the inner pipe to increase the heat transfer between the fluid and adsorbent. It was reported that the system could probably be commercially applied if an adsorbent bed with enhanced heat transfer was used.

A modified Carnot cycle for a heat engine using high temperature waste heat was presented by Wu and Schulden [46]. For performance analysis of the heat engine, the power per heat exchanger surface unit area was adopted. The relationship of the maximum obtainable specific power and the temperature range in which high-temperature waste heat engine operated was found. Meunier [47] discussed on the adsorption air-conditioning for automobiles and it was stated that in the global warming point of view, the car air-conditioning was an ideal solution for sorption systems to be competitive even with low COP. The difficulties faced by the technology are the need for light and compact units. This required efficiency improvement and heat transfer intensification in the adsorber to reduce the size and weight of the units.

Generally, the adsorption refrigeration technologies have been widely studied in academic field as well as in industry sectors [44]. It was confirmed that the engine exhaust gas could be a potential power source for adsorption refrigeration system. The introduction of the absorption refrigeration system in the engine exhaust system did not cause significant pressure drop in the exhaust flow. The specific fuel consumption was decreased with removal of other exhaust system components as the engine output power was increased [43]. However, there were also some limitations. One of limitations was the requirement of huge system due to the low adsorptive–desorptive capacity of the adsorbent. This resulted in the difficulties to install the system into automobiles. Hence, new synthetic or natural adsorbents with higher adsorptive capacity should have been invented to overcome this limitation. Additionally, commonly used adsorbates have low latent heat and high boiling point which cause low cooling effect. New type of adsorbates with less environmental impact should be used.

4. Principle of basic adsorption cycle

Air-conditioning is required all over the world to provide thermal comfort. This resulted in the increase amount of greenhouse gases emitted to our environment. It is vital to reduce the use of primary energy or use renewable energy for sustainable development of global energy [48]. The reduction of primary energy can be achieved by utilization of waste thermal energy [49]. Adsorption cycle has distinct advantage over other refrigeration systems in its ability to be driven by heat of relatively low, near-environmental temperature [48].

Heating and cooling due to adsorption cycles can be a good alternative to classical vapour-compression machines because solid/vapour sorption can use the non-polluting refrigerants and they have no moving parts which make the machine silent. Additionally, no maintenance is needed. As compared with liquid absorption systems, adsorption cooling units are much more attractive because they can operate at temperature levels where liquid absorption systems cannot work [50].

Generally, basic adsorption cycle can be represented by using Clapeyron ($\ln P$ versus $-1/T$) diagram as shown in Fig. 7. The cycle of adsorption refrigeration consists of two periods

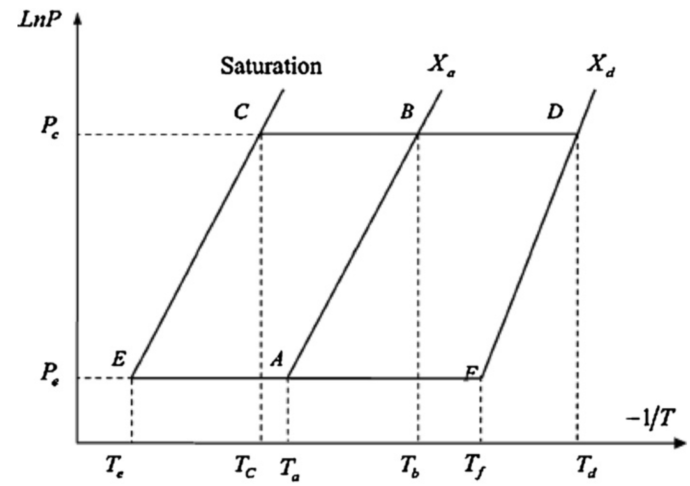

Fig. 7. Clapeyron diagram ($\ln P$ versus $-1/T$) of ideal adsorption cycle [51].

which are the heating–desorption–condensation period and the cooling–adsorption–evaporation period. During the heating–desorption–condensation period, the solar collector which consists of adsorbent bed and refrigerant will collect sunlight. When the temperature of the adsorbent bed rises to T_b, the vapour pressure of the desorbed refrigerants reaches the condensing pressure, P_c. The desorbed refrigerant vapour is condensed in the condenser and flows into the evaporator. The maximum temperature T_d can be obtained as the temperature of adsorbent bed continues to rise because of solar heating. During the cooling–adsorption–evaporation period, the temperature drops and the adsorbent bed is cooled. The temperature decreases from T_d to T_f. The refrigerant begins to evaporate and is re-adsorbed by the adsorbent bed [51].

5. Modification of activated carbon

Activated carbon has been used for thousands of years and has now become extremely versatile adsorbent due to its highly developed internal surface area and porosity. Activated carbon with high surface area is widely used in numerous fields, such as fuel gas storage, gas separation, super capacitor and catalysis. The adsorptive properties of carbon are well known long before the terms active and activated carbon had been developed or doped. The adsorption capacity as one of the most important properties is directly determined by the pore size distribution and is also strongly influenced by the surface functionality [52].

One of the attractive approaches for enhancement of heavy metal removal is the surface modification of activated carbon. According to Chen et al. [53], for different surface functional groups, different heavy metal ions would have different affinities. Generally, modification can be performed by adsorbing foreign organic compounds on the surfaces of carbon. It is well known that organic compounds are able to be effectively adsorbed by activated carbon in aqueous solutions and thus leads to immobilization of organic compounds on the carbon surface.

Nowadays, increasingly stringent regulations have required the generation of better quality product waters by treatment of industrial effluents that can be more easily reused or disposed of without altering or damaging the environment. A wide range of treatment technologies is being developed and optimized for a variety of applications in many different industries [54]. Great efforts have been done by voluminous researchers to study the influence of precursor and the preparation conditions on the pore characteristics and adsorption properties of activated carbon. However, only

Table 2
Technical advantages and disadvantages of existing modification techniques [55].

Modification	Treatment	Advantages	Disadvantages
Chemical characteristics	Acidic	Increases acidic functional groups on AC surface. Enhances chelation ability with metal species	May decrease BET surface area and pore volume Has adverse effect on uptake of organics May give off undesired SO_2 (treatment with H_2SO_4) or NO_2 (treatment with HNO_3) gases
	Basic	Enhances uptake of organics	May, in some cases, decrease the uptake of metal ions
	Impregnation of foreign material	Enhances in-built catalytic oxidation capability	May decrease BET surface area and pore volume
Physical characteristics	Heat	Increases BET surface area and pore volume	Decreases oxygen surface functional groups
Biological characteristics	Bioadsorption	Prolongs AC bed life by rapid oxidation of organics by bacteria before the material can occupy adsorption sites	Thick biofilm encapsulating AC may impede diffusion of adsorbate species

a few attempts so far have been made to study the effect of modification of activated carbon through chemical activation process [52].

Activated carbon is capable of distributing chemicals on its large hydrophobic internal surface due to the inert porous carrier ability and thus making it accessible to reactants. More and more researches on activated carbon modification are gaining prominence. It is well noted that activated carbon is effective to act as adsorbent for a wide range of contaminants. Recent researches have placed emphasis on modifying the physical and chemical attributes. Thus, it is very important to understand various factors which can influence the adsorption capacity of activated carbon prior to their modifications. All these factors must be tailored to the activated carbon specific physical and chemical attributes to enhance their affinities toward metal, inorganic or organic species. These factors include the specific surface area, pore size distribution, pore volume and presence of surface functional groups [55].

Zhao et al. [56] reported that the activated carbon treated by oxidation had higher adsorption property on Cr (VI) than that of the raw activated carbon. In their work, activated carbons were modified by chemical surface treatments with HNO_3, H_2O_2 and $Fe(NO_3)_3$ in order to obtain modified activated carbons having different surface properties. The samples treated by means of $Fe(NO_3)_3$ solution with the concentration of 10% as the oxygen agent subsequent to heat treatment showed the optimum adsorption property.

As reported by Chingombe et al. [57], different modes of modification of the activated carbon led to samples with different chemical characteristics. Modification by oxidation led to the fixation of weakly acidic functional groups as indicated by FTIR, pH titration results, sodium capacity and zeta potential results. Organic chemical reaction could be used to modify the activated carbon surface since it consisted of condensed aromatic structures. The reaction site was most likely to occur on the aliphatic side chains of the carbon when modified by oxidation because these sites were highly susceptible to oxidation. The oxidation processes, however produced some by-products in the form of humic substances which could be extracted by sodium hydroxide solution. They modified activated carbon by thermal and chemical methods and reported that nitric acid oxidation of the raw sample produced product with weakly acidic functional group.

Yin et al. [55] made a review on modification of activated carbon for enhancing contaminants uptakes for aqueous solutions and they reported that the oxidative treatment of activated carbon was very favourable for enhancing uptakes of metal ions while thermal treatment of activated carbon was generally favourable for enhancing adsorption of organic compounds from aqueous solutions since basic characteristic of the activated carbon was amplified at high temperature condition. Table 2 shows the technical advantages and disadvantages of existing modification techniques [55].

6. Conclusions

Most of the studies reported in the literature focused on the use of readily available commercial activated carbons for the application in adsorption refrigeration systems. The activated carbon modification process would be a potential alternative rather than finding new adsorbents for future development. It is expected that the modification process is able to overcome some of the limitations of the adsorbents. Research has shown that adsorption technology has a promising potential for competing with conventional absorption and vapour compression technologies. More research and effort are recommended for industrial development of adsorption air-conditioning system.

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